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Assistant Commissioner for Patents
Washington, DC 20231

Sir:

Transmitted herewith for filing is the patent application of

Inventor(s): KIMURA, Keizo; YABUKI, Yoshiharu; NAKAI, Yasufumi

For: DIAMINOSTILBENE DERIVATIVES

Enclosed are:

- ☒ A specification consisting of Thirty-seven (37) pages
- ☐ () sheet(s) of formal drawings
- ☒ An Assignment of the invention
- ☐ Certified Copy of Priority Document(s)
- ☒ Executed Declaration (☒ Original ☐ Photocopy)
- ☐ A statement (☐ Original ☐ Photocopy) to establish small entity status under 37 C.F.R. § 1.9 and 37 C.F.R. § 1.27
- ☐ Preliminary Amendment
- ☐ Information Disclosure Statement, PTO-1449 and reference(s)
- ☐ Other: _____

The filing Fee has been calculated as shown below:


			LARGE ENTITY	SMALL ENTITY
BASIC FEE			\$710.00	\$355.00
	NUMBER FILED	NUMBER EXTRA	RATE FEE	RATE FEE
TOTAL CLAIMS	9-20=	0	x 18 = \$0.00	x 9= \$0.00
INDEPENDENT CLAIMS	3-3=	0	x 80 = \$0.00	x40= \$0.00
<input type="checkbox"/> MULTIPLE DEPENDENT CLAIMS PRESENTED			+ \$270.00	+ \$135.00
TOTAL			\$710.00	\$0.00

- ☒ No filing Fee is enclosed
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Attachments

DIAMINOSTILBENE DERIVATIVES

5

FIELD OF THE INVENTION

10 The present invention relates to a 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative which is favorably employable in an aqueous fluorescent brightening solution, an aqueous photographic silver halide emulsion, an aqueous solution for processing a photographic silver halide-containing material. The invention further relates to use of the 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative for
15 brightening a variety of materials with fluorescence.

BACKGROUND OF THE INVENTION

20 Tamehiko Noguchi describes in Journal of Society of Organic Synthetic Chemistry (Yuki Gosei Kagaku Kyokai-shi), vol.19, p.920 (1961) and vol.20, p.64 (1962) that 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivatives are useful as fluorescent brightening agents.

25 United States Patents No. 2,875,058, No. 2,933,390, and No. 2,945,762 describe 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivatives are employable as additives for a photographic silver halide emulsion.

30 German Patent (DE) No. 1,945,316 discloses 4,4'-bis-(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivatives which show high fluorescent brightening effect on cellulose fibers. The disclosed derivatives have a sulfoethylamine substituent group on the 2-position of
35 its triazine ring and additionally a morpholine or alkanolamine substituent group on the 4-position. Examples of

the alkanolamines are monoethanolamine, methylethanolamine, diethanolamine, isopropanolamine, and diisopropanolamine.

5 The 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivatives to be employed in the form of aqueous solutions such as photographic silver halide emulsions and aqueous solutions for processing photographic silver halide-containing material are preferably well soluble in water or an aqueous solution. In more
10 detail, the derivatives should be rapidly dissolved in an aqueous medium and then should be hardly deposited during the storage of the aqueous solution.

Japanese Patent Provisional Publications No.6-329,936 and No.6-332,127 disclose 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivatives
15 which are employable as fluorescent brightening agents for an aqueous solution for processing photographic silver halide material. The disclosed derivatives have high solubility in the aqueous solution and are hardly deposited even when the processing solution is kept at low
20 temperatures. The latter 6-332,127 publication indicates that a preferred compound is such derivative that the triazine ring is substituted on its 2-position with ethylamine having a sodium sulfonate salt [therefore,
25 four sodium sulfonate groups are introduced into the derivative] and further substituted on its 4-position with an alkanolamine (e.g., 2-methylethanolamine).

SUMMARY OF THE INVENTION

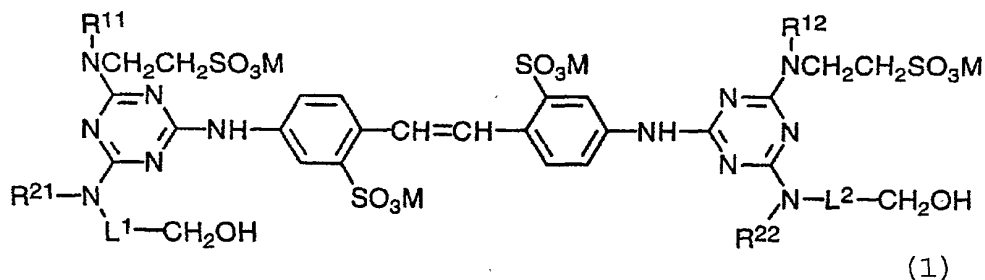
30 According to the studies of the present inventors, the known 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivatives do not show satisfactory solubility in an aqueous medium from the viewpoints of
35 practical use of the fluorescent brightening agent.

It is an object of the present invention to provide

4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivatives which show increased solubility in an aqueous medium.

As a result of further studies performed by the inventors, it has been discovered that the desired high solubility is attained by introducing into the 4-position of the triazine ring of the 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative an amino group having an alkylene substituent of 2 to 8 carbon atoms in which the alkylene substituent has a hydroxyl group or a hydroxyalkyl group of 1 to 3 carbon atoms as a substituent or has an intervening ether bonding.

Accordingly, the present invention resides in a 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative having the following formula (1):



in which

each of R¹¹ and R¹² independently is a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, or an alkyl group having 1 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, sulfo, and alkoxy;

R²¹ is a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkyl group having 1 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, sulfo, and alkoxy, an aryl group having 6 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, carboxyl, alkyl, or alkoxy, or a group represented by the formula

of $-L^1-CH_2OH$ wherein L^1 is an alkylene group having 2 to 8 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl and hydroxylalkyl having 1 to 3 carbon atoms or which has an intervening ether bonding;

R^{22} is a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, sulfo, and alkoxy, an aryl group having 6 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, carboxyl, alkyl, or alkoxy, or a group represented by the formula of $-L^2-CH_2OH$ wherein L^2 is an alkylene group having 2 to 8 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl and hydroxylalkyl having 1 to 3 carbon atoms or which has an intervening ether bonding; and

M is a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, ammonium group, or pyridinium group.

The 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivatives of the invention is included in the general formula (SR) of the diaminostilbene compound for fluorescent brightening agent which is disclosed in the aforementioned Japanese Patent Provisional Publication No.6-332127. However, the specifically defined 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivatives of the invention are not described in the publication.

The present invention further resides in an aqueous solution containing a 4,4'-bis(1,3,5-triazinylamino)-stilbene-2,2'-disulfonic acid derivative of the above-mentioned formula (1).

The invention furthermore resides in a method of brightening a surface of material with fluorescence which

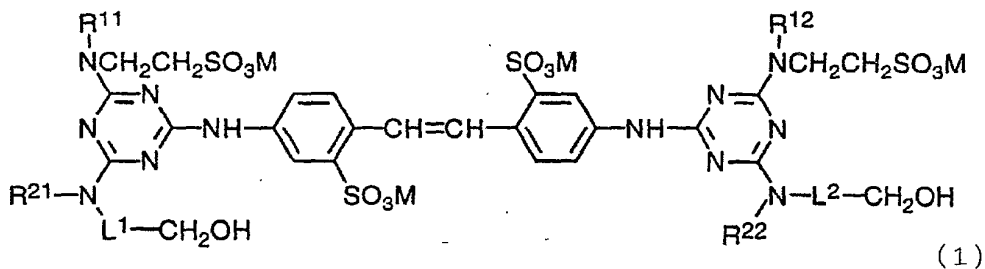
comprises applying a 4,4'-bis(1,3,5-triazinylamino)-stilbene-2,2'-disulfonic acid derivative of the formula (1) onto the surface of material.

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DETAILED DESCRIPTION OF THE INVENTION

The 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivatives of the invention is represented, as mentioned above, by the following formula (1):

10



15

In the formula (1), an alkyl group for R¹¹ and R¹² has 1 to 20 carbon atoms, preferably 1 to 8 carbon atoms, more preferably 1 to 4 carbon atoms. The alkyl group can be a straight chain alkyl group, a branched chain alkyl group, or a cyclic alkyl group. The alkyl group can have one or more substituent groups. Examples of the substituent groups include a hydroxyl group, a sulfo group, and an alkoxy group. The alkoxy group preferably has such alkyl group as mentioned above.

20

Examples of the alkyl groups for R¹¹ and R¹² include methyl, ethyl, n-propyl, isopropyl, n-octyl, 2-hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl, 2-sulfoethyl, 2-methoxyethyl, 2-(2-hydroxyethoxy)ethyl, 2-[2-(2-hydroxyethoxy)ethoxy]ethyl, and 2-(2-[2-(2-hydroxyethoxy)ethoxy]ethoxy)ethyl.

30

Each of R¹¹ and R¹² preferably is hydrogen, methyl, ethyl, n-propyl, n-butyl, or 2-sulfoethyl, and more preferably hydrogen, methyl, ethyl, or 2-sulfoethyl. Most preferred is hydrogen or atom.

35

Examples of the alkyl groups for R²¹ and R²² are those

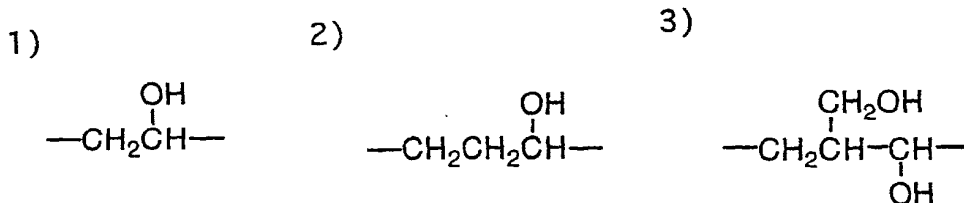
described hereinbefore for R^{11} and R^{12} . Preferred examples of R^{21} and R^{22} include hydrogen, methyl, ethyl, n-propyl, isopropyl, 2-hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl, 2,3-dihydroxypropyl, 2-sulfoethyl, 2-(2-hydroxyethoxy)ethyl, and 2-[2-(2-hydroxyethoxy)ethoxy]ethyl.

More preferred examples include hydrogen, methyl, ethyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2,3-dihydroxypropyl, and 2-(2-hydroxyethoxy)ethyl. Most preferred are hydrogen and methyl.

The aryl group for R^{21} and R^{22} has 6 to 20 carbon atoms, preferably 6 to 10 carbon atoms, more preferably 6 to 8 carbon atoms. The aryl group can have one or more substituents. Examples of the substituents include a hydroxyl group, a carboxyl group, an alkyl group, and an alkoxy group. The alkyl group and alkoxy group of the substituent can be the same as those described hereinbefore for R^{11} and R^{12} . Examples of the substituted and unsubstituted aryl groups for R^{21} and R^{22} include phenyl, naphthyl, 4-hydroxyphenyl, 3,5-dicarboxyphenyl, 4-methoxyphenyl, and 3-isopropylphenyl. The aryl group preferably is phenyl or 4-hydroxyphenyl.

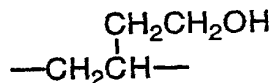
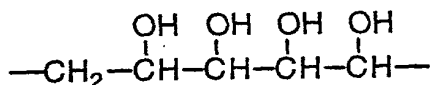
The alkylene group for L^1 and L^2 is an alkylene group having 2 to 8 carbon atoms which has, as a substituent, a hydroxyl group or a hydroxyalkyl group having 1 to 3 carbon atoms. Otherwise, the alkylene group has an ether bonding which intervenes the alkylene chain at an optional position.

Preferred examples of the alkylene group for L^1 and L^2 include those of the following formulas 1) to 5):



4)

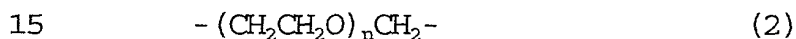
5)



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More preferred are those of the above-mentioned formulas 1) to 4), namely, alkylene groups having one or more hydroxyl substituent groups. Most preferred are those of the formulas 1) and 4).

Other preferred examples of the alkylene group for L¹ and L² include that represented by the following formula (2):

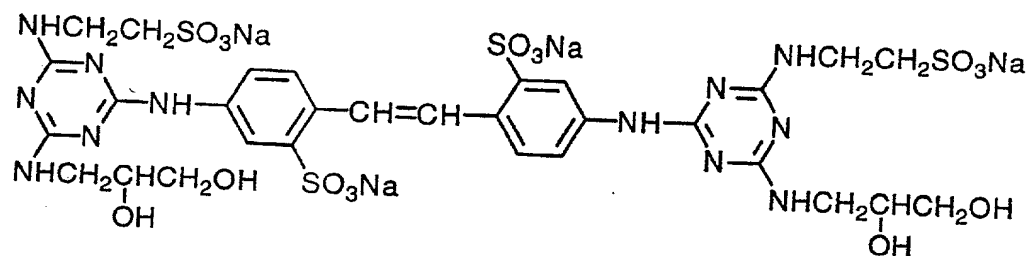


in which n is an integer of 1 to 3, preferably 1 or 2. Most preferably, n is 1.

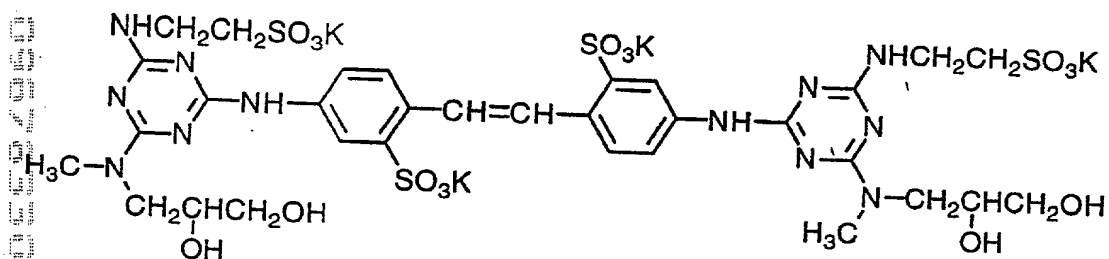
In the formula (1), M is a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, ammonium group, or pyridinium group. Examples of the alkali metal atoms include Li, Na, K, Rb, Cs, and Fr. Examples of the alkaline earth metal atoms include Ca, Sr, Ba, and Ra. Preferred are Na and K. Examples of the ammonium groups include triethylammonium and tetrabutylammonium.

Representative examples of the formula (1) of the invention are illustrated below:

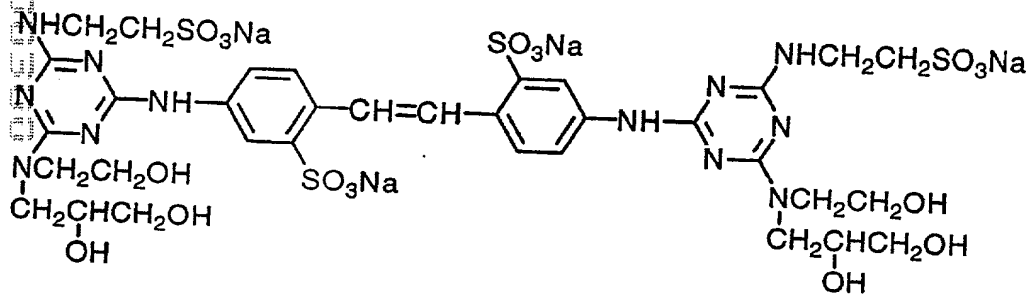
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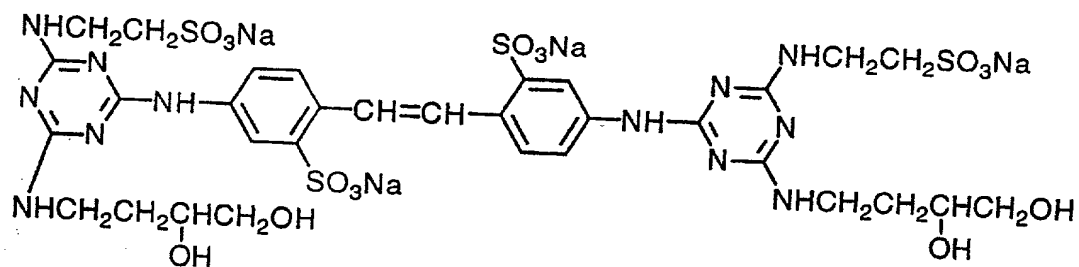
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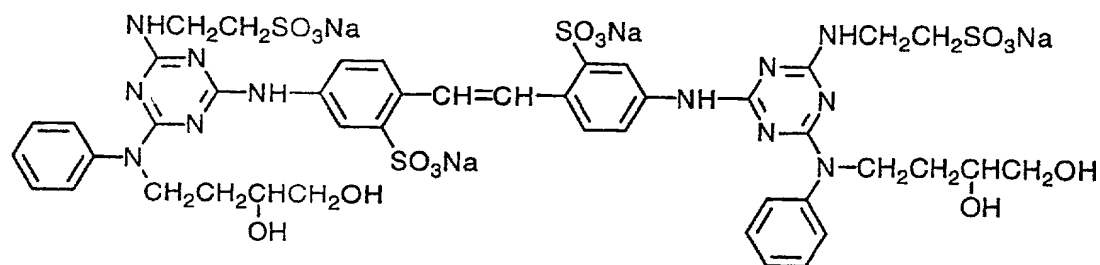
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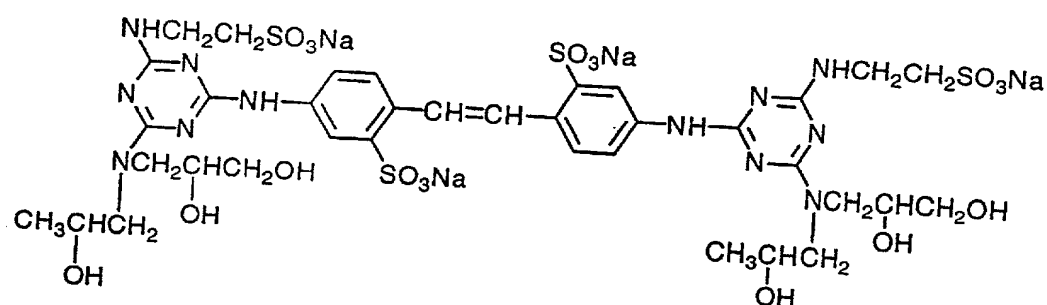
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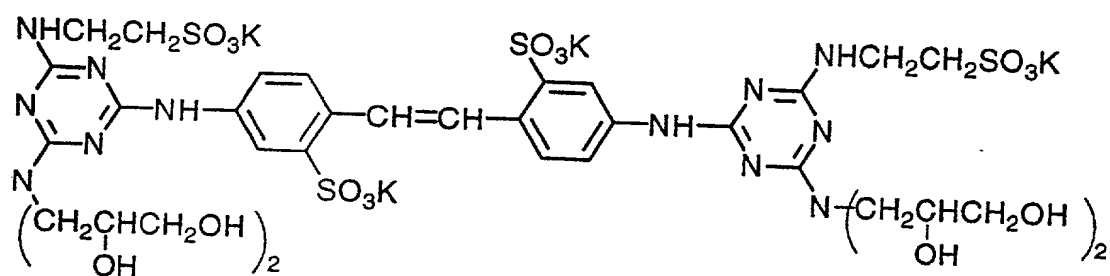
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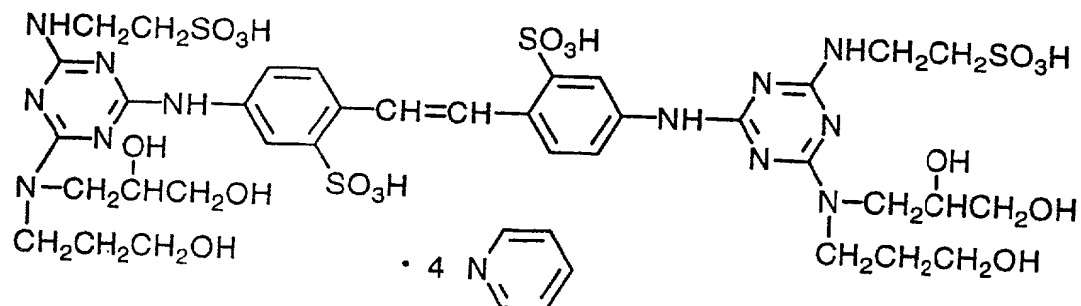
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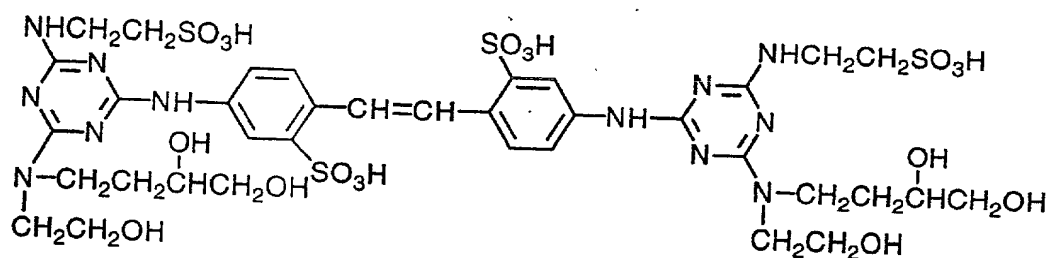
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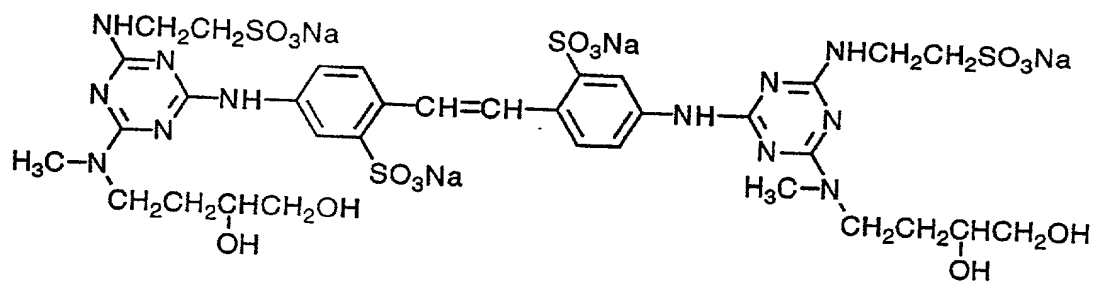
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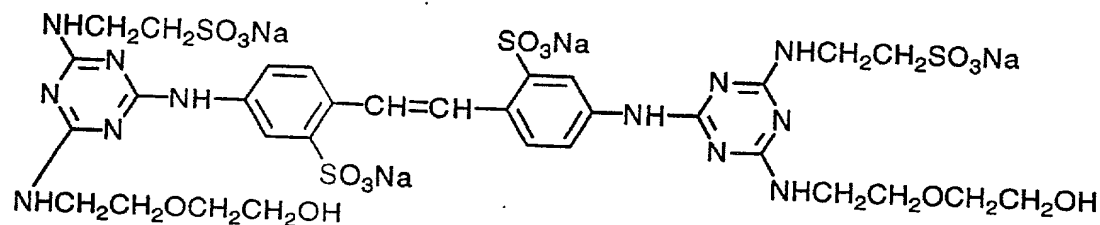
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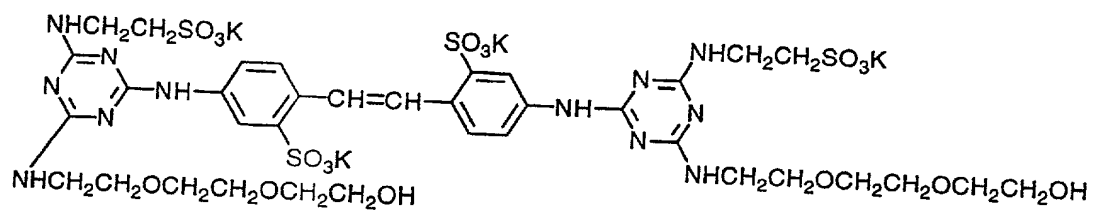
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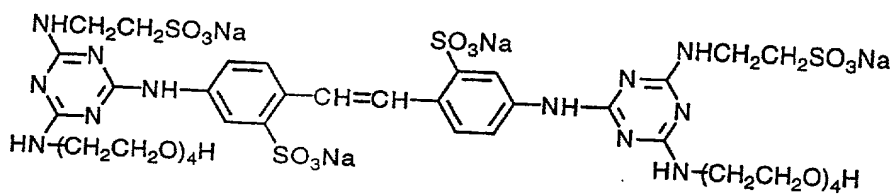
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I-12



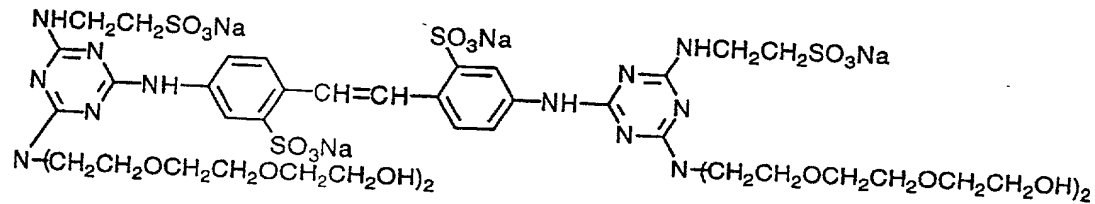
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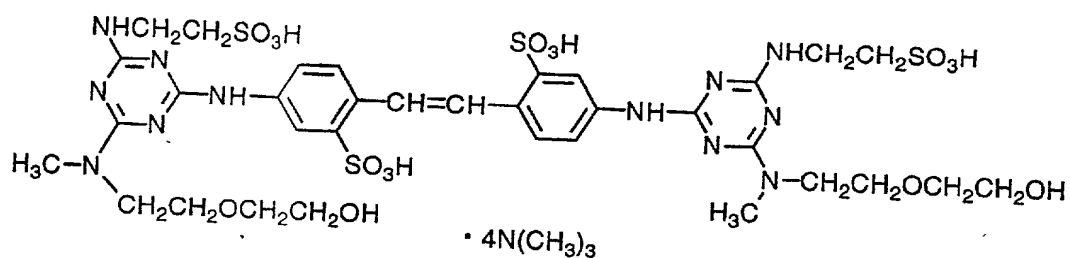
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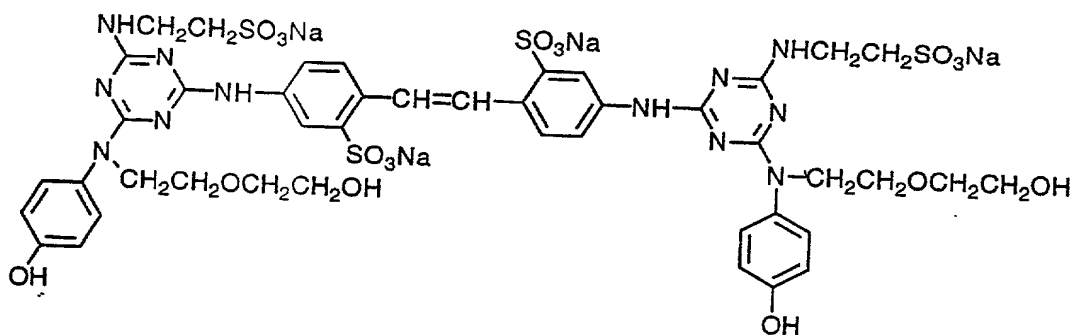
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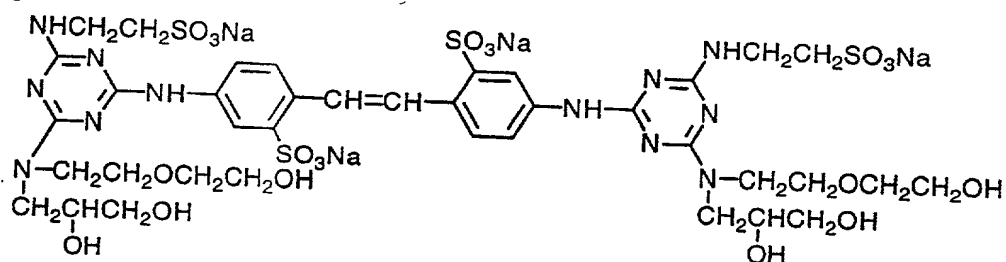
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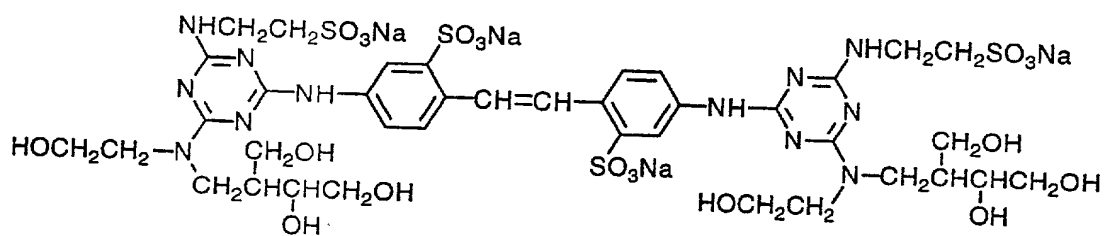
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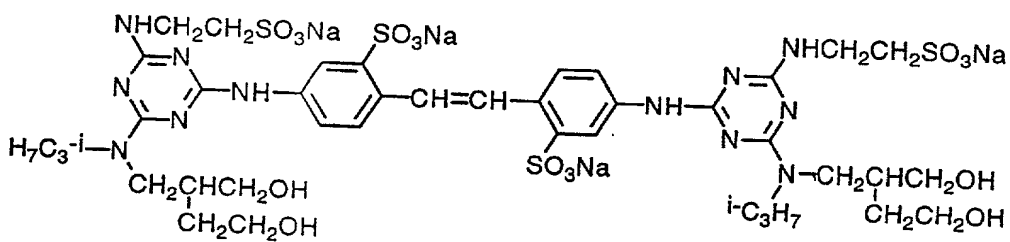
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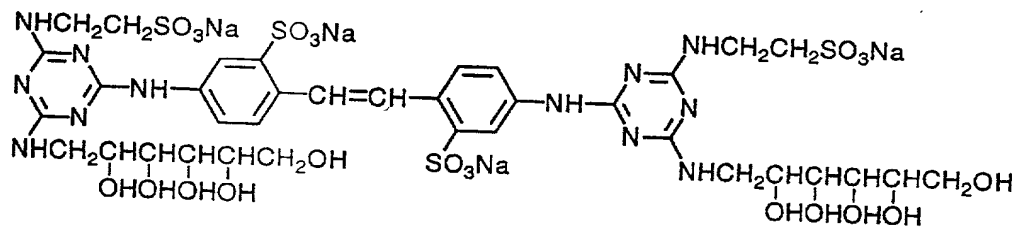
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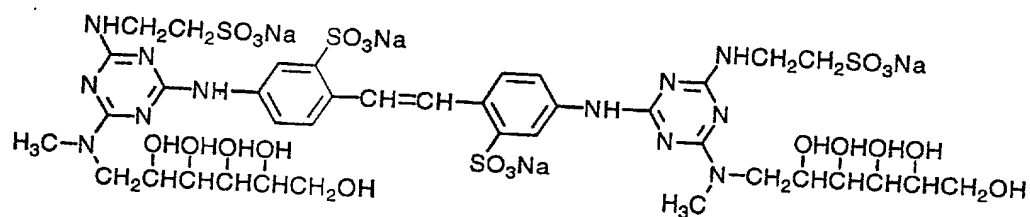
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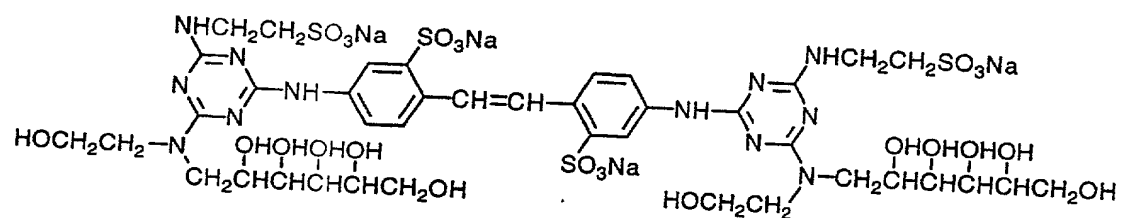
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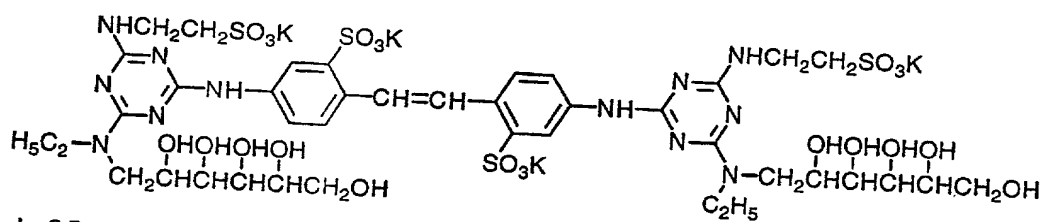
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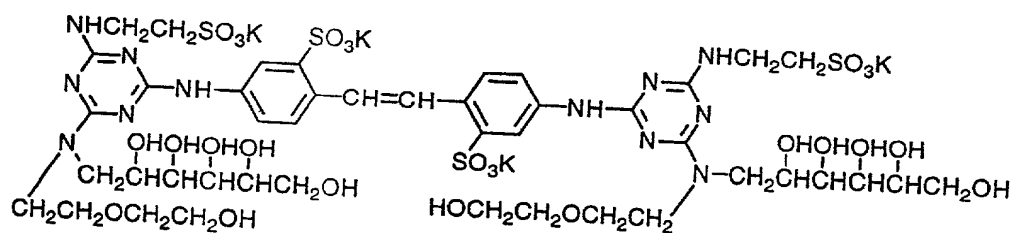
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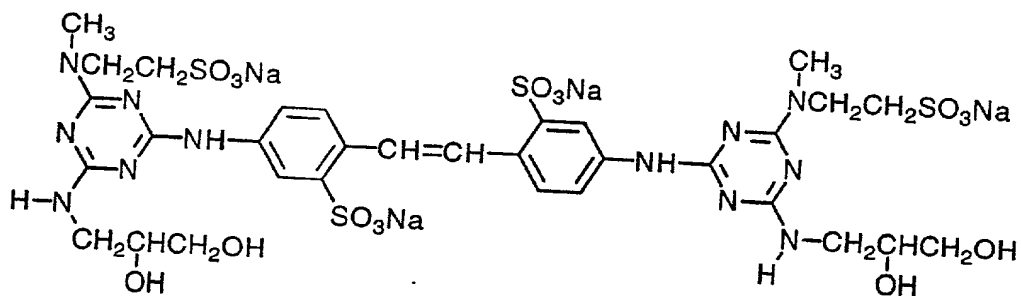
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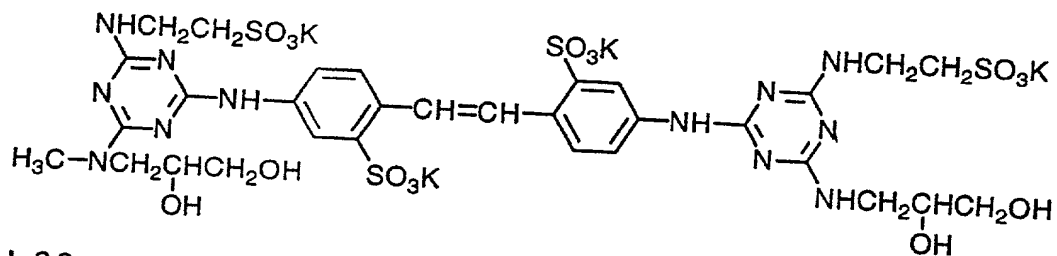
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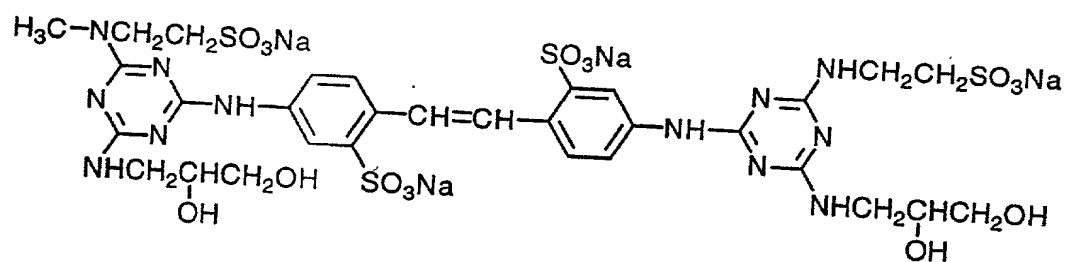
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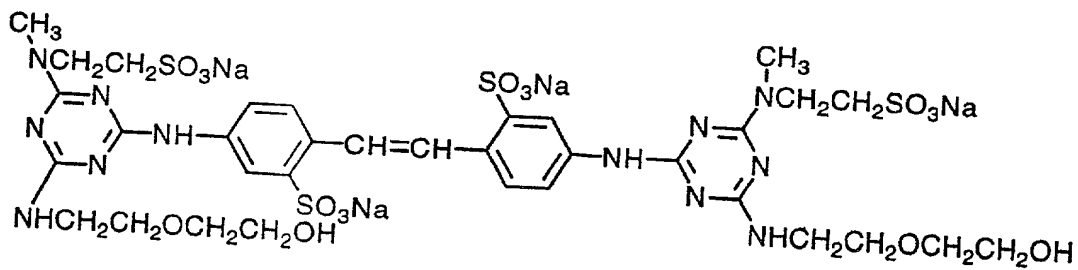
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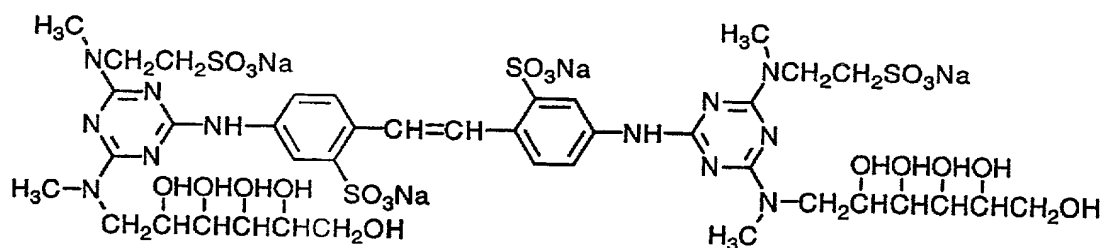
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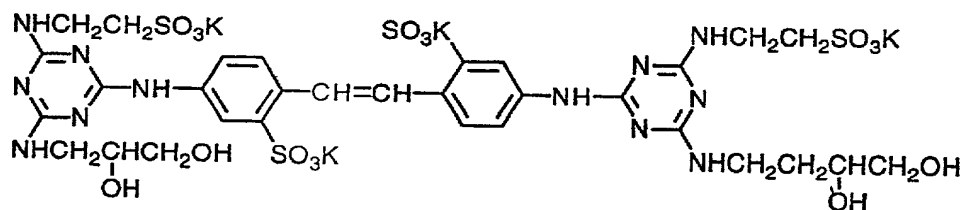
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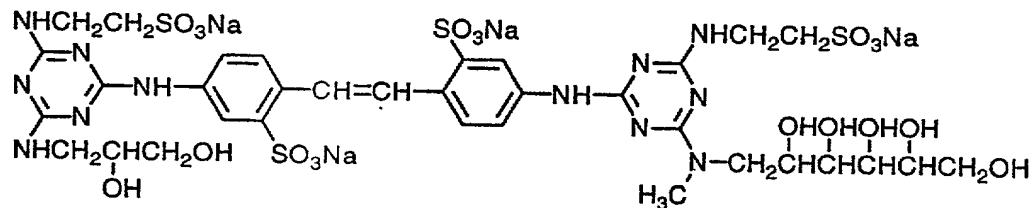
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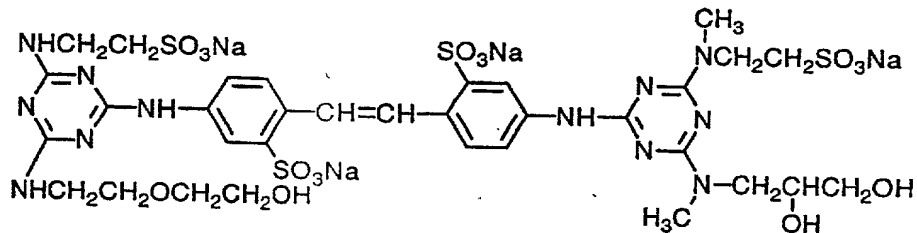
I-31



I-32



I-33



When the alkylene group for L¹ or L² of the formula (1) has a hydroxyl or hydroxyalkyl substituent and contains in its structure two or more asymmetric carbon atoms to which the substituent is attached, there are a plurality of stereoisomers having the same formula. Any of the isomers can be employed singly or in combination.

The 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative of the formula (1) can be prepared by referring to the descriptions of Journal of Society of Organic Synthetic Chemistry, vol. 17, page 528 (1959) [written by Hirotsugu Matsui] and Japanese Patent No. 2,618,748.

In more detail, the compound of the formula (1) can be prepared by the steps of reacting a diaminostilbene derivative with cyanuric chloride, reacting the resulting 4,4'-bistriazinylaminostilbene derivative with taurine, and finally reacting the resulting product with hydroxyalkylamine. Otherwise, a process starting from a dialkylaminostilbene derivative can be adopted.

The reaction can be performed in a solvent such as water or an organic solvent (e.g., alcohol, ketone, ether or amide). Water and water-miscible organic solvents are preferred. The reaction solvent can be a mixture of appropriate solvents. Preferred is an aqueous acetone solvent. Generally, a base is employed in the reaction. Examples of the bases include organic bases such as triethylamine, pyridine, and 1,8-diazabicyclo[5,4,0]-7-undecene, and inorganic bases such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium hydrogen carbonate, and sodium hydride. The inorganic bases such as sodium hydroxide, potassium hydroxide, sodium carbonate and potassium carbonate are preferably employed. The reaction is generally performed at a temperature in the range of -20°C to 120°C, preferably -10°C to 90°C. In more detail, the reaction in the first step is preferably performed at a temperature of

-10C° to 10C°; the reaction in the second step is preferably performed at a temperature of 0C° to 40C°; and the reaction in the third is preferably performed at a temperature of 50C° to 90C°.

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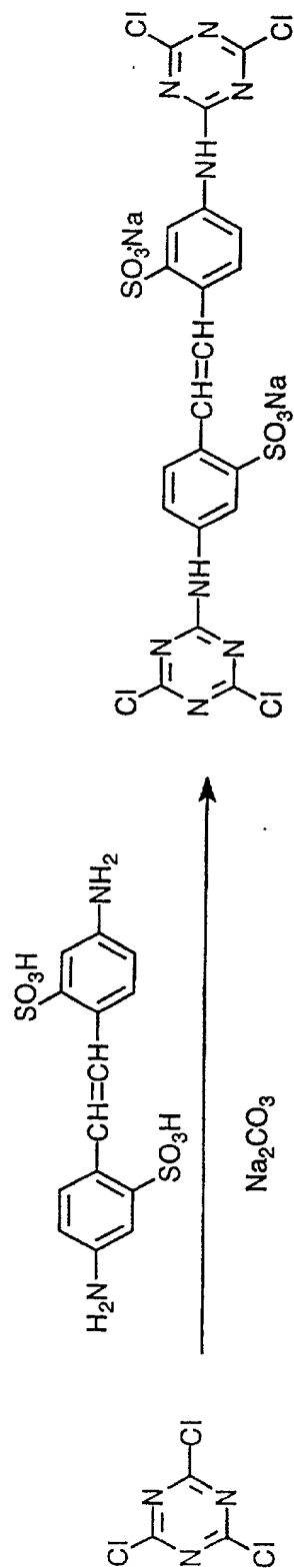
The present invention is further described by the following non-restricting examples.

[Example 1]

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The aforementioned compound (I-1) of the invention was prepared according to the following scheme:

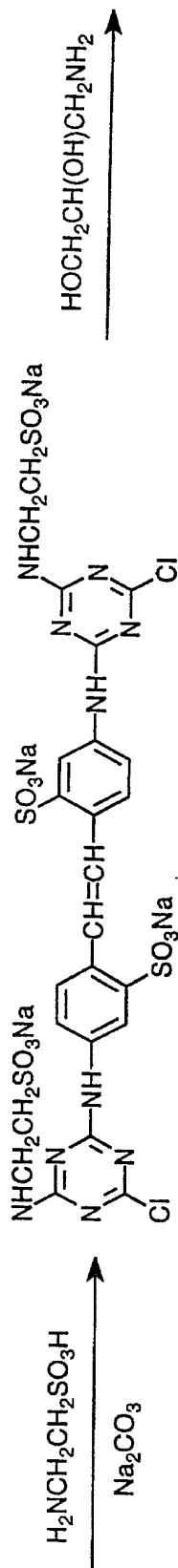
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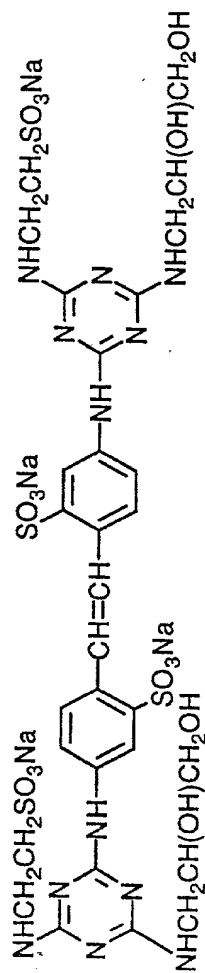
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Compound (I)

1) Preparation of Compound 3

In a three-necked flask were placed 103.5 g of Compound 1 and 680 mL of acetone. The content was chilled to -5°C by placing the flask in an ice-acetone bath. To the chilled content was dropwise added under stirring an aqueous solution of 101.9 g of Compound 2 and 58.3 g of sodium carbonate in 960 mL of water for a period of one hour. The temperature of the flask content increased to -1°C. After the dropwise addition was complete, the ice-acetone bath was removed, and the flask content was further stirred for one hour. The precipitated crystalline product was collected on filter by suction, to obtain the desired Compound 3. Thus obtained product was submitted to the next step without drying and purifying.

2) Preparation of Compound 4

In a three-necked flask were placed the Compound 3 obtained above and 1.9 L of water. The content was stirred on a water bath, and to the stirred content was added 68.8 g of taurine. Further, an aqueous solution of 58.3 g of sodium carbonate in 275 mL of water was dropwise added for a period of one hour under stirring. After the dropwise addition was complete, the water bath was removed and the stirring was continued for 3 hours. To the stirred content was added 550 g of sodium chloride, and the stirring is continued for one hour. The precipitated crystalline product was collected on filter by suction, to obtain the desired Compound 4. Thus obtained product was submitted to the next step without drying and purifying.

3) Preparation of the compound (I-1)

In a three-necked flask were placed the Compound 4 obtained above and 825 mL of water. The content was stirred at room temperature, and to the stirred content was dropwise added 125.3 g of Compound 5 at room temperature, while the stirring was continued. After the dropwise addition was complete, the content was stirred at an

inner temperature of 85°C for 3 hours. The reaction mixture was concentrated in a rotary evaporator. When the residual content reduced to approximately 800 mL, a crystalline product precipitated and the concentration procedure was stopped. The content was then stirred with chilling with ice, and the precipitated crystalline product was collected on filter by suction. To thus obtained crystalline product was added 1.5 L of methanol, and the resulting mixture was stirred for one hour under reflux. The reaction mixture was cooled to room temperature, and subjected to filtration using suction, to obtain 206.0 g (yield: 72%) of the desired Compound (I-1).

$$\lambda_{\max}(\text{H}_2\text{O}) = 346.3 \text{ nm } (\epsilon = 4.83 \times 10^4)$$

The obtained product of Compound (I-1) had a purity of 96.0% (determined by liquid chromatography).

The liquid chromatography was carried out under the following conditions:

Column: TSK-gel ODS-80 (available from Tosoh Co., Ltd.)

Eluents:

Eluent A (20 mL of PIC A reagent, available from Waters Corp., was added to 1 L of water)

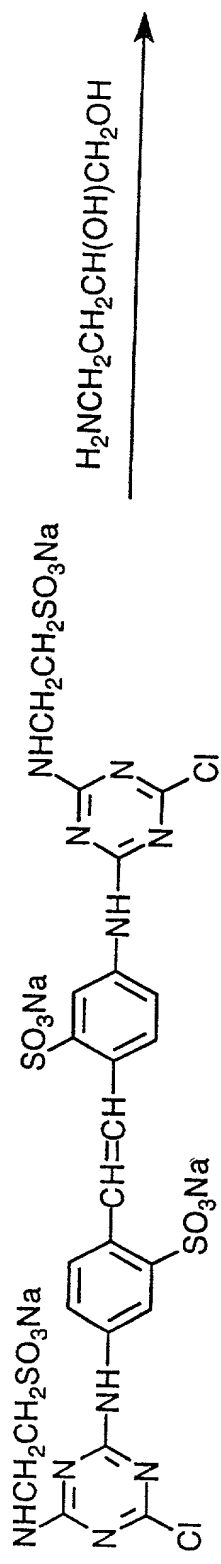
Eluent B (20 mL of PIC A reagent was added to a mixture of 800 mL of methanol and 200 mL of water)

Eluent A/Eluent B = 50/50 (0 min.) →
0/100 (35 min.)

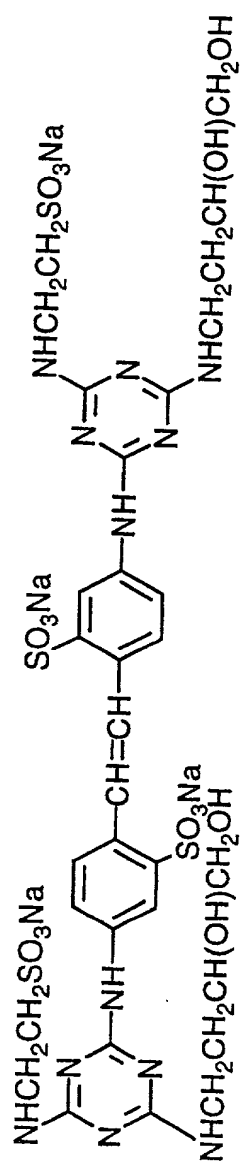
Detecting wavelength: 346 nm
The purity was determined from a peak area of the chromatographic chart.

[Example 2]

The aforementioned compound (I-4) of the invention was prepared according to the following scheme:



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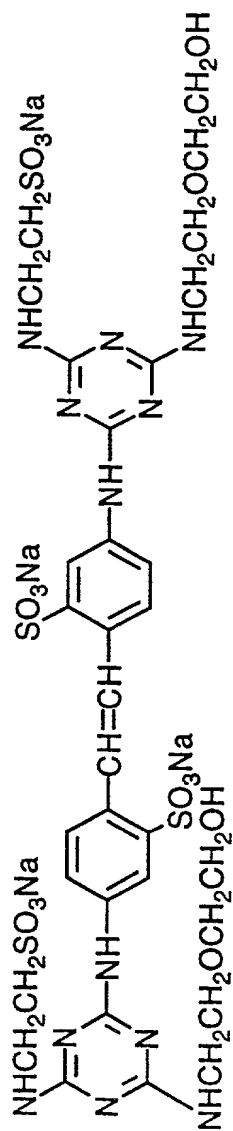
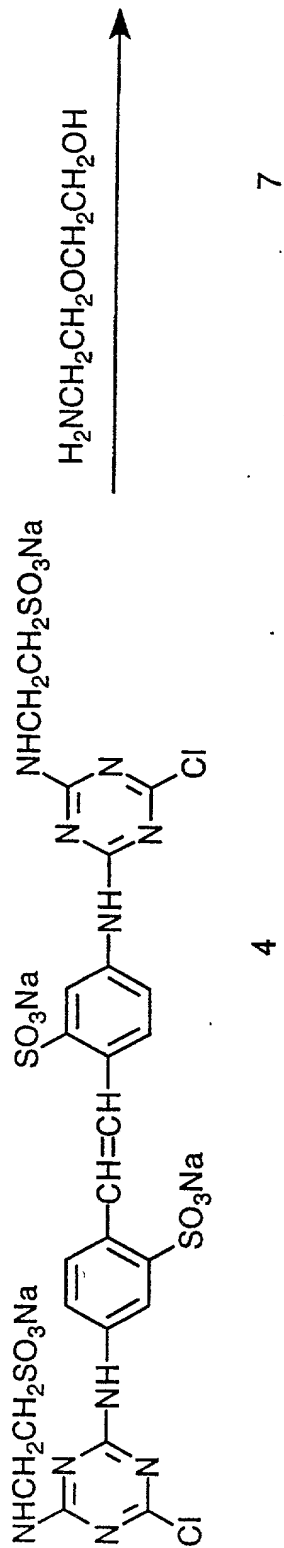
In a three-necked flask were placed Compound 4 which had been prepared in the same manner as in Example 1 (i.e., same scale and same synthetic process) and 825 mL of water. The content was stirred at room temperature, and to the stirred content was dropwise added 144.6 g of Compound 6 at room temperature for 10 minutes, while the stirring was continued. After the dropwise addition was complete, the content was stirred at an inner temperature of 85°C for 3 hours. The reaction mixture was concentrated in a rotary evaporator. When the residual content reduced to approximately 900 mL, a crystalline product precipitated and the concentration procedure was stopped. The content was then stirred with chilling with ice, and the precipitated crystalline product was collected on filter by suction. To thus obtained crystalline product was added 1.5 L of methanol, and the resulting mixture was stirred for one hour under reflux with heating. The reaction mixture was cooled to room temperature, and subjected to filtration using suction, to obtain 216.5 g (yield: 78%) of the desired Compound (I-4).

$$\lambda_{\max}(\text{H}_2\text{O}) = 346.5 \text{ nm } (\epsilon = 4.77 \times 10^4)$$

The obtained product of Compound (I-4) had a purity of 94.4% (determined by liquid chromatography which was performed in the same manner as in Example 1).

[Example 3]

The aforementioned compound (I-11) of the invention was prepared according to the following scheme:



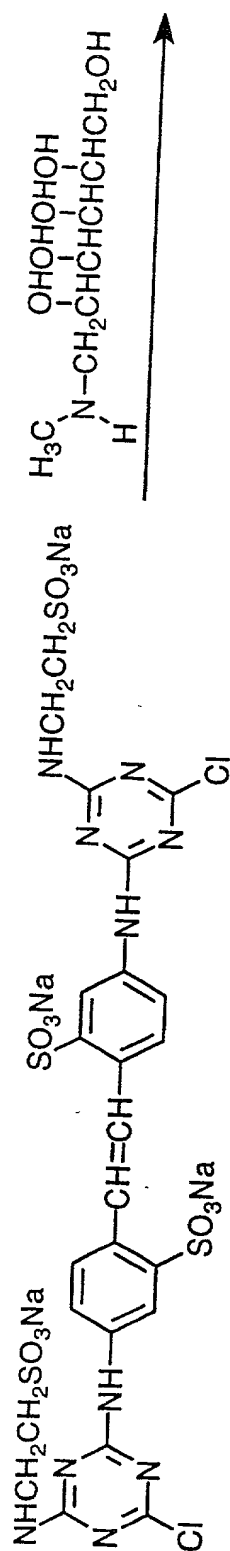
In a three-necked flask were placed Compound 4 which had been prepared in the same manner as in Example 1 (i.e., same scale and same synthetic process) and 825 mL of water. The content was stirred at room temperature, and to the stirred content was dropwise added 144.4 g of Compound 7 at room temperature for 10 minutes, while the stirring was continued. After the dropwise addition was complete, the content was stirred at an inner temperature of 85°C for 3 hours. The reaction mixture was concentrated in a rotary evaporator. When the residual content reduced to approximately 800 mL, a crystalline product precipitated and the concentration procedure was stopped. The content was then stirred with chilling with ice, and the precipitated crystalline product was collected on filter by suction. To thus obtained crystalline product was added 1.5 L of methanol, and the resulting mixture was stirred for one hour under reflux with heating. The reaction mixture was cooled to room temperature, and subjected to filtration using suction, to obtain 249.7 g (yield: 85%) of the desired Compound (I-11).

$$\lambda_{\max}(\text{H}_2\text{O}) = 354.5 \text{ nm } (\epsilon = 4.92 \times 10^4)$$

The obtained product of Compound (I-11) had a purity of 97.3% (determined by liquid chromatography which was performed in the same manner as in Example 1).

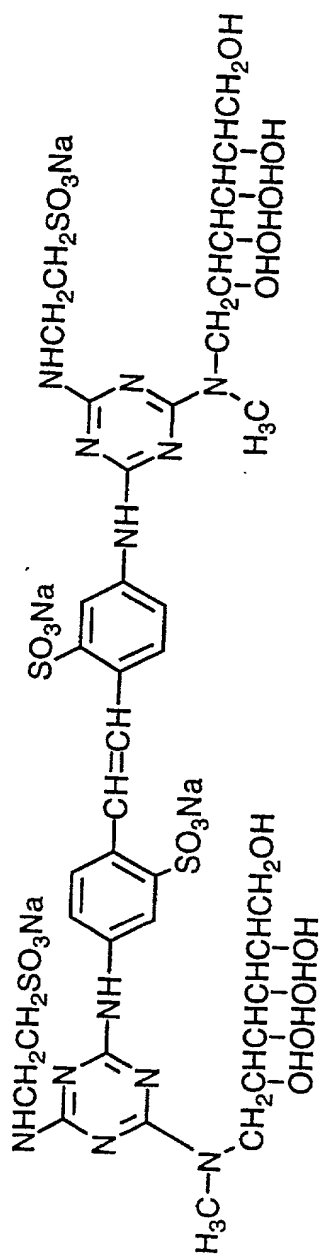
[Example 4]

The aforementioned compound (I-22) of the invention was prepared according to the following scheme:



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Compound (I-22)

In a three-necked flask were placed Compound 4 which had been prepared in the same manner as in Example 1 (i.e., same scale and same synthetic process) and 825 mL of water. The content was stirred at room temperature, and to the stirred content was dropwise added 268.5 g of Compound 8 at room temperature for 10 minutes, while the stirring was continued. After the dropwise addition was complete, the content was stirred at an inner temperature of 85°C for 3 hours. The reaction mixture was concentrated in a rotary evaporator. When the residual content reduced to approximately 900 mL, a crystalline product precipitated and the concentration procedure was stopped. The content was then stirred with chilling with ice, and the precipitated crystalline product was collected on filter by suction. To thus obtained crystalline product was added 1.5 L of methanol, and the resulting mixture was stirred for one hour under reflux with heating. The reaction mixture was cooled to room temperature, and subjected to filtration using suction, to obtain 302.9 g (yield: 88%) of the desired Compound (I-22).

$$\lambda_{\max}(\text{H}_2\text{O}) = 348.6 \text{ nm } (\epsilon = 4.36 \times 10^4)$$

The obtained product of Compound (I-22) had a purity of 96.1% (determined by liquid chromatography which was performed in the same manner as in Example 1).

[Examples 5 and 6]

The aforementioned Compound (I-2) and compound (I-12) were prepared in manner similar to those described in Examples 1 to 4.

[Example 7]

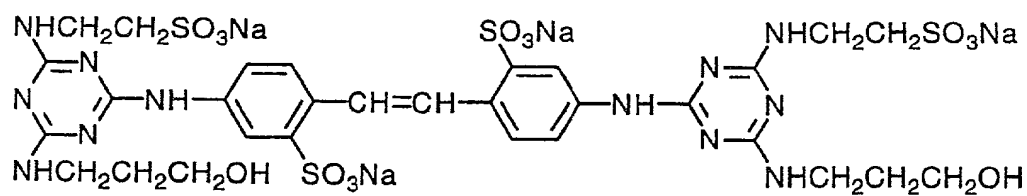
Compounds I-1, I-2, I-4, I-11, I-12, and I-22 obtained above, and the Comparison Compounds a, b, c and d were subjected to evaluation of solubility in water.

Water (100 mL) was added to 20 g of each sample, and

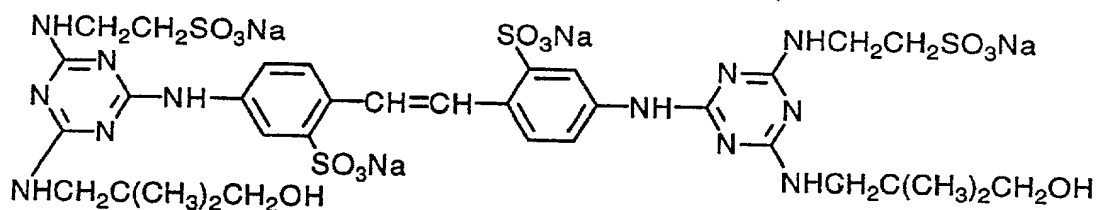
the mixture was placed on a warm bath (at 40°C), and stirred using a magnetic stirrer, so that the added sample was dissolved in the warm water. Then, the obtained aqueous solution was placed on an ice bath under stirring.

The conditions of the aqueous mixture in the dissolving procedure and the aqueous solution on the ice bath were observed for evaluating solubility in water at 40°C and 0°C. The results are seen in the following Table.

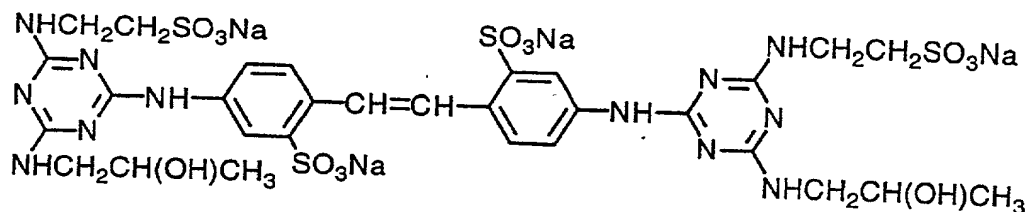
Compound	Solubility at 40°C	Solubility of 0°C
Comp. I-1	dissolved within 120 sec.	No deposition within 180 sec.
Comp. I-2	dissolved within 150 sec.	No deposition within 180 sec.
Comp. I-4	dissolved within 150 sec.	No deposition within 180 sec.
Comp. I-11	dissolved within 120 sec.	No deposition within 180 sec.
Comp. I-12	dissolved within 140 sec.	No deposition within 180 sec.
Comp. I-4	dissolved within 140 sec.	No deposition within 180 sec.
Comp. a	some insoluble remained at 300 sec.	Not examined
Comp. b	some insoluble remained at 300 sec.	Not examined
Comp. c	dissolved at 200 sec.	Deposition found at 120 sec.
Comp. d	dissolved at 180 sec.	Deposition found at 150 sec.



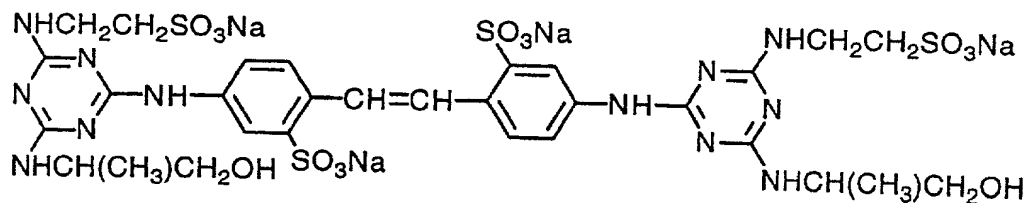
Comparison compound a



Comparison compound b



Comparison compound c
described in DE 1946316



Comparison compound d
described in Japanese Patent Application No.6-332127

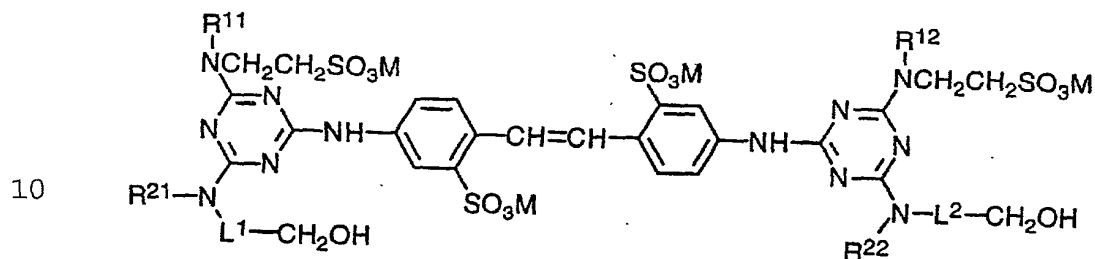
[Example 8]

In 1 mL of water was dissolved 10 mg of each of Compounds I-1, I-2, I-3, I-4, I-5, I-11, I-12, I-13, I-14,
5 I-21, and I-22. The aqueous solution was diluted with methanol to give 5 mL of an aqueous methanol solution.

The resulting aqueous methanol solution was applied on to a filter paper sheet, and the paper sheet was dried. Thus treated filter paper sheet was irradiated
10 with a UV light ($\lambda = 254$ nm). All paper sheets emitted blue fluorescence.

What is claimed is:

1. 4,4'-Bis(1,3,5-triazinylamino)stilbene-2,2'-
5 disulfonic acid derivative having the following formula:



in which

15 each of R^{11} and R^{12} independently is a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, or an alkyl group having 1 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, sulfo, and alkoxy;

20 R^{21} is a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkyl group having 1 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, sulfo, and alkoxy, an aryl group having 6 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms which has one or more substituents
25 selected from the group consisting of hydroxyl, carboxyl, alkyl, or alkoxy, or a group represented by the formula of $-\text{L}^1-\text{CH}_2\text{OH}$ wherein L^1 is an alkylene group having 2 to 8 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl and hydroxylalkyl
30 having 1 to 3 carbon atoms or which has an intervening ether bonding;

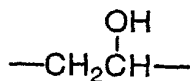
35 R^{22} is a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkyl group having 1 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, sulfo, and alkoxy, an aryl group having 6 to 20 carbon atoms, an aryl group having 6

to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, carboxyl, alkyl, or alkoxy, or a group represented by the formula of $-L^2-CH_2OH$ wherein L^2 is an alkylene group having 2 to 8 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl and hydroxylalkyl having 1 to 3 carbon atoms or which has an intervening ether bonding; and

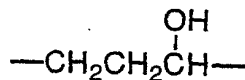
M is a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, ammonium group, or pyridinium group.

2. 4,4'-Bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative of claim 1, wherein at least one of L^1 and L^2 is a divalent group which is represented by one of the following formulas 1) to 5):

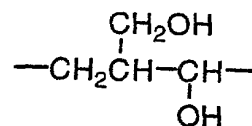
1)



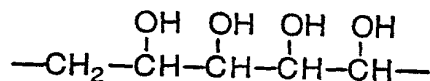
2)



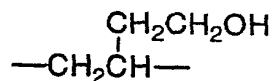
3)



4)

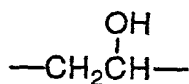


5)

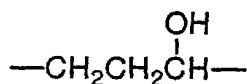


3. 4,4'-Bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative of claim 1, wherein at least one of L^1 and L^2 is a divalent group which is represented by one of the following formulas 1) to 4):

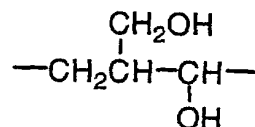
1)



2)

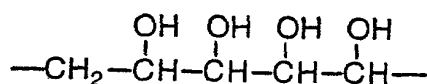


3)



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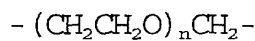
4)



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4. 4,4'-Bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative of claim 1, wherein at least one of L¹ and L² is a divalent group which is represented by the following formula:

15



in which n is an integer of 1 to 3.

20

5. 4,4'-Bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative of claim 4, wherein n in the formula is 1 or 2.

25

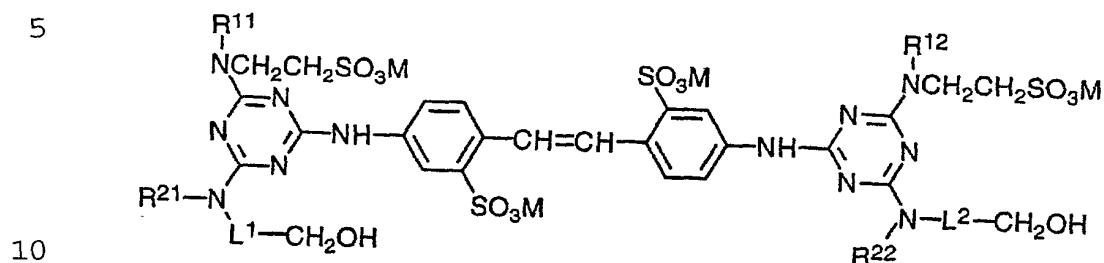
6. 4,4'-Bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative of claim 1, wherein each of R¹¹ and R¹² in the formula independently is hydrogen or methyl.

30

7. 4,4'-Bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative of claim 1, wherein each of R²¹ and R²² in the formula independently is hydrogen, methyl, ethyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2,3-dihydroxypropyl, 2-(2-hydroxyethoxy)-ethyl, 2-[2-(2-hydroxyethoxy)ethoxy]ethyl, phenyl, or 4-hydroxyphenyl.

35

8. An aqueous solution in which a 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative having the following formula is dissolved in water:



in which

each of R^{11} and R^{12} independently is a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, or an alkyl group having 1 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, sulfo, and alkoxy;

R^{21} is a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkyl group having 1 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, sulfo, and alkoxy, an aryl group having 6 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, carboxyl, alkyl, or alkoxy, or a group represented by the formula of $-L^1-CH_2OH$ wherein L^1 is an alkylene group having 2 to 8 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl and hydroxylalkyl having 1 to 3 carbon atoms or which has an intervening ether bonding;

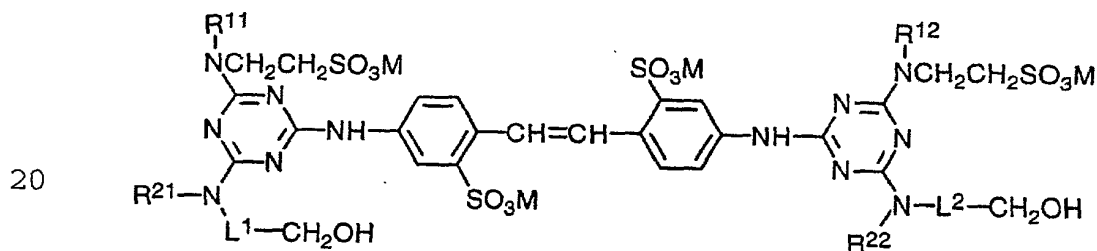
R^{22} is a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkyl group having 1 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, sulfo, and alkoxy, an aryl group having 6 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, carboxyl,

alkyl, or alkoxy, or a group represented by the formula
of $-L^2-CH_2OH$ wherein L^2 is an alkylene group having 2 to 8
carbon atoms which has one or more substituents selected
from the group consisting of hydroxyl and hydroxylalkyl
5 having 1 to 3 carbon atoms or which has an intervening
ether bonding; and

M is a hydrogen atom, an alkali metal atom, an alka-
line earth metal atom, ammonium group, or pyridinium
group.

10

9. A method of brightening a surface of material
with fluorescence which comprises applying onto the sur-
face an aqueous solution in which a 4,4'-bis(1,3,5-tri-
azinylamino)stilbene-2,2'-disulfonic acid derivative
15 having the following formula is dissolved in water:



in which

each of R^{11} and R^{12} independently is a hydrogen atom,
25 an alkyl group having 1 to 20 carbon atoms, or an alkyl
group having 1 to 20 carbon atoms which has one or more
substituents selected from the group consisting of hy-
droxyl, sulfo, and alkoxy;

R^{21} is a hydrogen atom, an alkyl group having 1 to 20
30 carbon atoms, an alkyl group having 1 to 20 carbon atoms
which has one or more substituents selected from the
group consisting of hydroxyl, sulfo, and alkoxy, an aryl
group having 6 to 20 carbon atoms, an aryl group having 6
to 20 carbon atoms which has one or more substituents
35 selected from the group consisting of hydroxyl, carboxyl,
alkyl, or alkoxy, or a group represented by the formula

of $-L^1-CH_2OH$ wherein L^1 is an alkylene group having 2 to 8 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl and hydroxylalkyl having 1 to 3 carbon atoms or which has an intervening ether bonding;

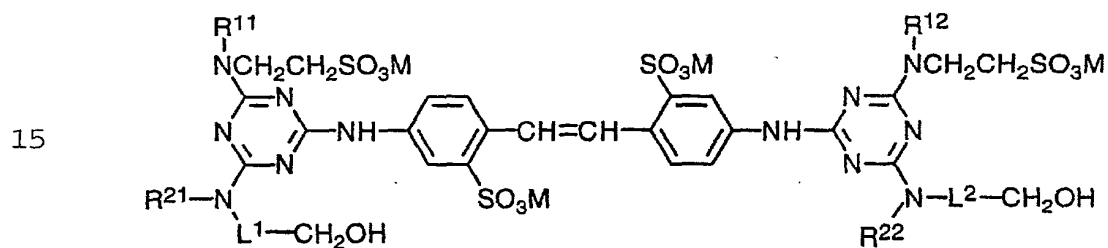
R^{22} is a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkyl group having 1 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, sulfo, and alkoxy, an aryl group having 6 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl, carboxyl, alkyl, or alkoxy, or a group represented by the formula of $-L^2-CH_2OH$ wherein L^2 is an alkylene group having 2 to 8 carbon atoms which has one or more substituents selected from the group consisting of hydroxyl and hydroxylalkyl having 1 to 3 carbon atoms or which has an intervening ether bonding; and

M is a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, ammonium group, or pyridinium group.

5

ABSTRACT OF THE DISCLOSURE

10 The following 4,4'-bis(1,3,5-triazinylamino)stilbene-2,2'-disulfonic acid derivative is well soluble in water:



20 in which each of R¹¹ and R¹² is hydrogen, or a specifically substituted or unsubstituted alkyl group; each of R²¹ and R²² is hydrogen, a specifically substituted or unsubstituted alkyl group, a specifically substituted or unsubstituted aryl group; M is hydrogen, alkali metal, alkaline earth metal, ammonium, or pyridinium.

**COMBINED DECLARATION AND POWER OF ATTORNEY
FOR PATENT AND DESIGN APPLICATIONS**

ATTORNEY DOCKET NO.
2016-165P

**PLEASE NOTE:
YOU MUST
COMPLETE THE
FOLLOWING:**

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated next to my name; that I verily believe that I am the original, first and sole inventor (if only one inventor is named below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Insert Title:

DIAMINOSTILBENE DERIVATIVES

**Fill in Appropriate
Information -
For Use Without
Specification
Attached:**

the specification of which is attached hereto. If not attached hereto,

the specification was filed on _____ as
United States Application Number _____; and /or

the specification was filed on _____ as PCT
International Application Number _____; and was
amended under PCT Article 19 on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I do not know and do not believe the same was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application, that the same was not in public use or on sale in the United States of America more than one year prior to this application, that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months (six months for designs) prior to this application, and that no application for patent or inventor's certificate on this invention has been filed in any country foreign to the United States of America prior to this application by me or my legal representatives or assigns, except as follows.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

**Insert Priority
Information:
(if appropriate)**

Prior Foreign Application(s)

(Number)	(Country)	(Month/Day/Year Filed)	Priority Claimed
11-280694	Japan	09/30/1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
(Number)	(Country)	(Month/Day/Year Filed)	<input type="checkbox"/> Yes <input type="checkbox"/> No
(Number)	(Country)	(Month/Day/Year Filed)	<input type="checkbox"/> Yes <input type="checkbox"/> No
(Number)	(Country)	(Month/Day/Year Filed)	<input type="checkbox"/> Yes <input type="checkbox"/> No
(Number)	(Country)	(Month/Day/Year Filed)	<input type="checkbox"/> Yes <input type="checkbox"/> No

**Insert Provisional
Application(s):
(if any)**

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below.

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

All Foreign Applications, if any, for any Patent or Inventor's Certificate Filed More Than 12 Months (6 Months for Designs) Prior To The Filing Date of This Application:

**Insert Requested
Information:
(if appropriate)**

Country	Application No.	Date of Filing (Month/Day/Year)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

**Insert Prior U.S.
Application(s):
(if any)**

(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)
(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)

I hereby appoint the following attorneys to prosecute this application and/or an international application based on this application and to transact all business in the Patent and Trademark Office connected therewith and in connection with the resulting patent based on instructions received from the entity who first sent the application papers to the attorneys identified below, unless the inventor(s) or assignee provides said attorneys with a written notice to the contrary:

Terrell C. Birch	(Reg. No. 19,382)	Raymond C. Stewart	(Reg. No. 21,066)
Joseph A. Kolasch	(Reg. No. 22,463)	James M. Slattery	(Reg. No. 28,380)
Bernard L. Sweeney	(Reg. No. 24,448)	Michael K. Mutter	(Reg. No. 29,680)
Charles Gorenstein	(Reg. No. 29,271)	Gerald M. Murphy, Jr.	(Reg. No. 28,977)
Leonard R. Svensson	(Reg. No. 30,330)	Terry L. Clark	(Reg. No. 32,644)
Andrew D. Meikle	(Reg. No. 32,868)	Marc S. Weiner	(Reg. No. 32,181)
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full Name of First or Sole Inventor: Insert Name of Inventor Insert Date This Document is Signed Insert Residence Insert Citizenship Insert Post Office Address	GIVEN NAME	FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
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